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Polymers can Force Calcite to form via Amorphous Mineral Precursors — and Synchrotron X-ray Studies can Reveal the Details

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Scientists at Brookhaven National Laboratory in Upton, New York, and the University of Florida in Gainesville have used synchrotron x-ray scattering to monitor how mineral crystals and films form at an organic boundary surface, a process related to biological mineral formation. Beneath an organic monolayer, calcium carbonates crystallize rapidly from solution into calcite, but the addition of polymers produces an amorphous thin film and delays the conversion to crystalline calcite. The x-ray measurements reveal that the amorphous thin film forms through kinetic mechanisms rather than the previously assumed templating mechanism, where the atomic positions of organic functional groups match the lattice spacing of the mineral crystal.

In a process called biomineralization, some living organisms incorporate insoluble mineral compounds into their biological structures, creating biominerals that are usually hard but much less brittle than the inorganic (geological) minerals are. Such biominerals are all the more fascinating because of the wealth of minerals having the same composition but different crystal structures used by animals. For example, calcium carbonates (CaCO_3) are abundant geologically but mainly as the stable minerals calcite and aragonite. But numerous marine invertebrates incorporate a broader range of calcium carbonates into their shells, such as the metastable vaterite and unstable amorphous hydrated calcium carbonates.

To study the biomineralization mechanisms, we have assembled organic molecules on a supersaturated CaCO_3 solution. The cations (Ca^{2+}) in solution are attracted to the negatively charged monolayer of organic molecules at the surface, creating an ion-rich region which eventually crystallizes into one or more crystal forms of CaCO_3 (**figure 1**). Up to now, this process had never before been monitored by a quantitative structural probe.

For the first time, we have determined the cation binding by analyzing the x-ray reflectivity from the initially assembled film. We found that, in the presence of polyacrylic acid – a soluble polymer which may mimic the action of biomolecules – the number of calcium cations bound to the surface layer was 80% less than in the case without polymer. Thus, the acidic macromolecules affect biomineralization primarily by reducing the concentration of cations at the monolayer. Instead, the charged polymer concentrates the ions to form a metastable amorphous layer, from which they can begin to crystallize against the overlying organic monolayer.



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Without an appropriate organic template, this polymer-induced precursor initiates the formation of calcite homogeneously in solution, and, in some cases, we noticed that the amorphous precursor has a liquid-like consistency. This observation suggests that it may be possible for living organisms to "mold" biomineral crystals through a precursor mechanism. The organic substrate therefore controls the liquid-like or solid nature of the precursor material, a mechanism which may allow the fabrication of synthetic "biomimetic," or biomineral-inspired, materials.

At beam line X22B of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, New York, we have measured both x-ray reflectivity – sensitive to the surface-normal density profile of the film – and grazing-incidence diffraction – probing in-plane structure – during the 20-hour biomineralization process. The time series of reflectivity curves (**figure 2a**) displays interference patterns showing that a thick film grows beneath the organic monolayer. Fitting a structural model to this data indicates that the film has a density comparable to amorphous, hydrated CaCO_3 phases,

half as dense as the anhydrous crystalline forms.

During the 20-hour biomineralization process, diffraction patterns within the layer plane (**figure 2b**) show that the organic monolayer retains a tightly packed, two-dimensional structure, but no crystalline diffraction from the underlying mineral is observed.

These x-ray measurements provide important new information: Biomineralization can occur through an amorphous precursor, even when no structural alignment between the organic monolayer and the mineral is present. Also, simple variations in polymer concentration and supersaturation have pronounced effects on mineralization rate. These results are

in contrast to suggestions in the literature, which have relied, up to now, upon assumptions regarding the alignment of crystals to organic monolayer templates. Our study shows that in-situ structural probes are increasingly important in illuminating the mechanisms of biomineralization.

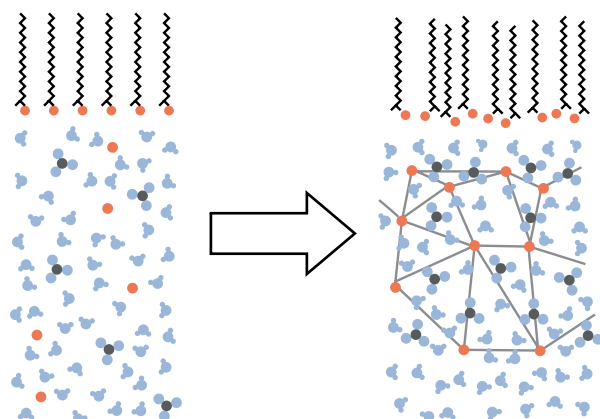


Figure 1. Scheme for biomineralization at an organic monolayer. A fatty acid, $\text{CH}_2(\text{CH}_3)_{18}\text{COOH}$, self-assembles at the surface of an aqueous layer supersaturated in calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions and containing dissolved poly(acrylic acid). At the negatively charged fatty acid headgroups, the ions that are sequestered by the polymer collect and heterogeneously form an amorphous hydrated mineral film, which reaches a thickness of more than 30 nanometers (or billionths of a meter) in 20 hours. The amorphous film subsequently crystallizes into calcite.

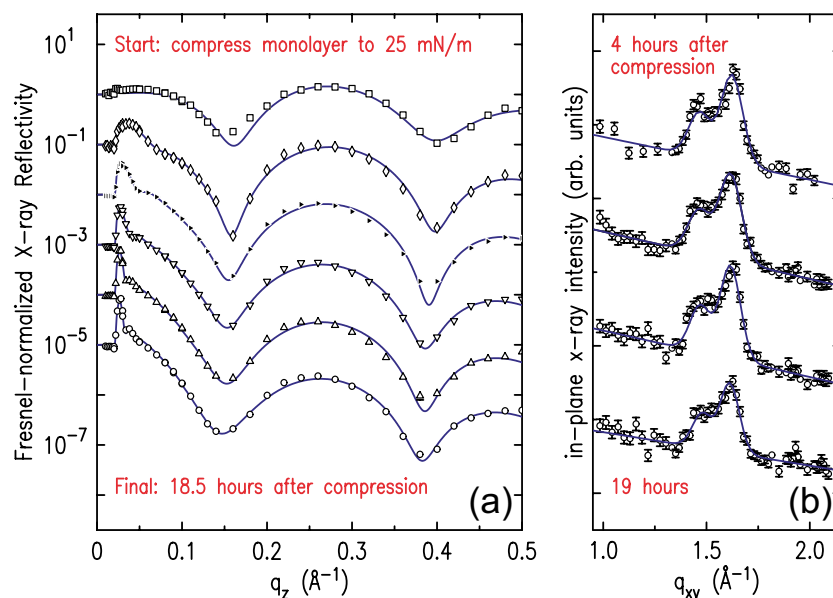


Figure 2. (a) Time series of normalized reflectivity curves from initial preparation of the sample through the growth of the mineral film. Oscillations in the data (symbols) are due to the reflection of x-rays from interfaces defined by the surface layers. Fit curves (lines) allow quantitative determination of the length scales and densities of both monolayer and mineral. The sharp peak near the origin is the main time-dependent feature, and provides a direct measure of the thickness of the mineral film. **(b)** Time series of in-plane scattering in a grazing incidence geometry, which is sensitive to the order of surface species within the layer plane. The observed peaks are consistent with tightly compressed fatty acid monolayers. Bragg diffraction peaks from crystalline calcium carbonate (CaCO_3) mineral species are not observed during this phase of mineral film growth, showing that the precursor film is amorphous.